

Unconventional carrier-mediated ferromagnetism above room temperature in ion-implanted (Ga, Mn)P:C

N. Theodoropoulou and A. F. Hebard*
*Department of Physics, University of Florida,
Gainesville, FL 32611-8440*

M.E. Overberg, C.R. Abernathy, and S.J. Pearton
*Department of Materials Science and Engineering,
University of Florida, Gainesville, FL 32611-8440*

S.N.G. Chu
Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974

R.G. Wilson
Consultant, Stevenson Ranch, CA 95131

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Ion implantation of Mn ions into hole-doped GaP has been used to induce ferromagnetic behavior above room temperature for optimized Mn concentrations near 3 at.%. The magnetism is suppressed when the Mn dose is increased or decreased away from the 3 at.% value, or when *n*-type GaP substrates are used. At low temperatures the saturated moment is on the order of one Bohr magneton, and the spin wave stiffness inferred from the Bloch-law $T^{3/2}$ dependence of the magnetization provides an estimate $T_c = 385\text{K}$ of the Curie temperature that exceeds the experimental value, $T_c = 270\text{K}$. The presence of ferromagnetic clusters and hysteresis to temperatures of at least 330K is attributed to disorder and proximity to a metal-insulating transition.

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The rather short interval between discovery of ferromagnetism in the Mn doped III-V semiconductor GaAs [1] and the demonstration of unique phenomena such as field-effect control of ferromagnetism [2], efficient spin injection to produce circularly polarized light [3, 4], and spin-dependent resonant tunneling [5], opens a rich and varied landscape for technological innovation in magnetoelectronics [6]. Although the Curie temperature, $T_c = 110\text{K}$, of (Ga,Mn)As is spectacularly high, it is not high enough, and any real breakthrough with respect to applications will require diluted magnetic semiconductors (DMS) which exhibit ferromagnetism above room temperature [6]. Already there are reports of room temperature ferromagnetism in the DMS chalcopyrite $\text{Cd}_{1-x}\text{Mn}_x\text{GeP}_2$ [7], (Ga,Mn)N formed by diffusion [8], and Co-doped ZnO [9] and TiO₂ anatase [10, 11].

In this letter we report on carrier-mediated ferromagnetism in (Ga,Mn)P, doped *p*-type with carbon (C), that persists to above room temperature. High T_c behavior is only observed for samples that are prepared at an optimal Mn concentration near 3 at.% on heavily p-doped GaP substrates. When electron-doped substrates are simultaneously implanted with the same Mn concentration, T_c is strongly suppressed. Hysteresis in the 3 at.% material extends to temperatures well above the temperature

where the dc susceptibility, $\chi(T)$, diverges and the “saturated” moment is observed to have strong temperature dependence. These observations suggest a percolation type of picture in which isolated ferromagnetic magnetic clusters, immersed in a background of paramagnetic moments, grow in size as the temperature is lowered until, at $T = T_c$, long-range order extends through the whole system. The characteristics, which we have observed and will describe below, thus reveal phenomenology that can be used to assess the relevance of distinct yet complementary theoretical viewpoints [12, 13, 14, 15].

The use of GaP as a host semiconductor for magnetic dopants is advantageous: it has a large bandgap (2.2eV), it is an important component of the AlGaInP materials system, which is used for visible light-emitting diodes and high speed electronics, and it is also nearly lattice-matched to Si, offering the possibility of combining DMS with conventional Si circuitry. Epitaxial films of (Ga,Mn)P have shown single-phase material up to Mn atomic concentrations of 9% and hysteretic magnetic behavior that persists up to 250K [16].

Two types of GaP substrates were used in these experiments. The first were bulk (100) substrates with nominally undoped *n*-type (10^{16}cm^{-3}) background carrier densities and the second were 0.4μm-thick epi layers

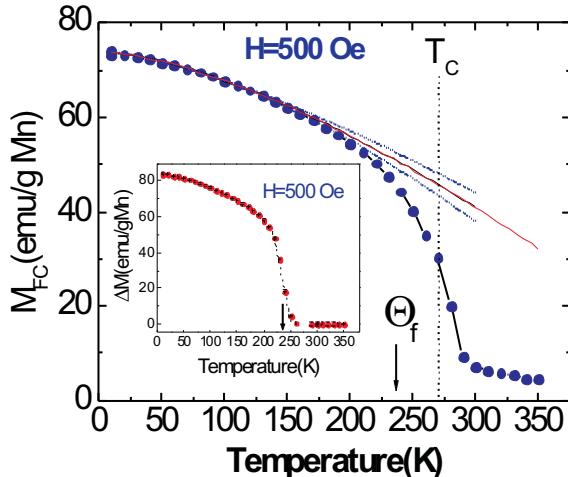


FIG. 1: Temperature dependence of field-cooled (FC) magnetization (per gram Mn) at at an applied field $H = 500\text{Oe}$. At low temperatures a Bloch law ($T^{3/2}$) dependence (solid line) was found. The dashed lines are 95% confidence bands. The dashed line at $T_c = 270\text{K}$ marks the field independent inflection point (Curie temperature) and the vertical arrows in the main panel and the inset mark the ferromagnetic Curie temperature, $\Theta_f = 236\text{K}$. Inset: Temperature dependence of the difference ΔM between field cooled (FC) and zero-field cooled (ZFC) magnetizations taken in a field of 500Oe.

grown by Gas Source Molecular Beam Epitaxy on top of GaP substrates. These layers were heavily C-doped ($p \approx 10^{20} \text{ cm}^{-3}$, 10^{-2}Ohm cm) using carbon tetrabromide (CBr_4) as the dopant source [17]. The samples were implanted with 250keV Mn^+ ions to doses of $3\text{-}5 \times 10^{16} \text{ cm}^{-2}$ at a temperature of 350C to maximize crystallinity [18]. These conditions produce relatively flat Mn concentration profiles with peak volume concentrations of 3 or 5 at.% over a projected $\approx 0.2\mu\text{m}$ depth in each sample. Following a rapid thermal anneal, the samples were characterized by transmission electron microscopy (TEM), selected area diffraction pattern analysis (SADP), and double crystal x-ray diffraction (DC-XRD) [19]. No evidence of secondary phase formation of GaMn or MnP was found. All magnetic measurements were made with a Quantum Design SQUID magnetometer with the applied field parallel to the film surface. Similar results were also obtained for perpendicular fields.

Shown in Fig. 1 is a plot of the temperature-dependent magnetization for the 3at.% ($\text{Ga}_{0.94}\text{Mn}_{0.06}\text{P}$) sample cooled in a field of 500Oe. A temperature independent diamagnetic contribution was subtracted from the background. In contrast to $(\text{Ga,Mn})\text{As}$ [20] the temperature-dependent magnetization has the classic convex outwards shape but with a substantial tail extending to higher temperatures. The Curie temperature $T_c = 270\text{K}$, indicated by the vertical dashed line, is defined as the inflection point and does not shift in position for similar data sets

taken in different fields and sample orientations.

At low temperatures the saturated moment, $M_0 = g\mu_BS$, is calculated to be about one Bohr magneton (μ_B) per Mn ion, thus implying that for a g -factor of 2 the spin $S = 1/2$. This value is a factor of five less than $S = 5/2$ expected for the half-filled d -band of divalent Mn, a discrepancy most likely arising because of strong antiferromagnetic coupling among the more closely spaced randomly positioned Mn ions [12]. The solid line is a three parameter fit to an expression of the form, $M(T) = M_0(1 - \alpha T^\eta)$, over the temperature range $T \leq 160\text{K}$. The observation of a Bloch law dependence with exponent $\eta = 3/2$ is expected for ferromagnets and reflects the presence of long-wavelength thermally excited spin waves. The dashed lines delineate the 95% confidence band for the best-fit parameters $\eta = 1.51(6)$ and $\alpha = 1.09(35) \times 10^{-4}$.

The inset of Fig. 1 shows the temperature-dependent difference $\Delta M = M_{FC} - M_{ZFC}$ between field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves taken at 500Oe. This subtraction advantageously eliminates para- and diamagnetic contributions and simultaneously indicates the presence of hysteresis if the difference is non-zero. It should be noted that the knee of this curve occurs at a lower temperature than the knee of the FC curve (main panel) and moves to even lower temperature at higher measuring fields. This trend can be understood by realizing that at a given temperature, $\Delta M = 0$ if the measuring field is higher than the maximum field at which hysteresis is observed in $M(H)$ loops acquired at the same temperature. Examples of such loops are shown in Fig. 2. Hysteresis with a coercive field $H_c = 100\text{Oe}$ is quite pronounced at 250K (lower panel) to fields as high as 600Oe . At lower fields, hysteresis similar to that

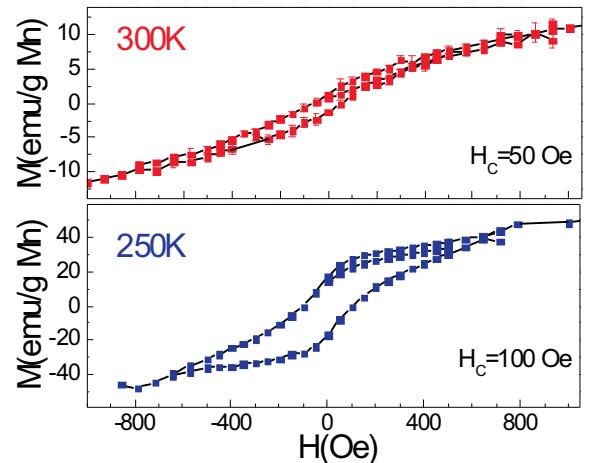


FIG. 2: Magnetization loops showing moderate hysteresis with coercive field, $H_c = 50\text{Oe}$ (upper panel) at 300K and a stronger hysteresis with $H_c = 100\text{Oe}$ (lower panel) at 250K .

shown at 300K in the upper panel of Fig. 2 extends to 330K.

The FC-ZFC subtraction is particularly effective when there are small amounts of ferromagnetic material in the presence of a large diamagnetic and/or paramagnetic background. This situation ensues when *n*-type rather than *p*-type GaP is implanted with 3at.% Mn (Fig. 3, upper panel) or *p*-type GaP is implanted with 5at.% Mn (Fig. 3, lower panel). These data show that the maximum FC-ZFC difference, ΔM , is reduced by a factor of 15-20 and the T_c by a factor of ≈ 6 , over the temperature range 300K to near 50K. Accordingly, an optimized T_c is extremely sensitive to both the carrier and Mn concentrations. Furthermore, ferromagnetic impurity phases such as MnGa ($T_c > 300K$) [20] and MnP ($T_c = 291K$) [21] are not responsible, since an increase of Mn leads to less, not more, magnetism, and the formation and amount of such impurity phases should also be independent of hole-doping level.

Although our observations confirm conventional ferromagnetism at low temperatures, the magnetic behavior is considerably more complicated at higher temperatures as shown by the Fig. 4 plots of the temperature-dependent inverse dc susceptibility $\chi^{-1}(T)$ (main panel) and saturation moment $M_s(T)$ (inset). The data for these plots were obtained at selected temperatures by recording $M_{ZFC}(H)$ to the maximum available field of 5T. A temperature-dependent diamagnetic contribution that varied less than 1% over the temperature range studied was subtracted from the data. We used a Langevin functional dependence to determine $\chi = dM_{ZFC}/dH$

and $M_s(T)$ at each temperature. We identify the ferromagnetic Curie temperature $\Theta_f = 236K$ (vertical arrow) by a linear extrapolation of $\chi^{-1}(T)$ to zero. The hysteresis and accompanying saturated moment extend with diminishing magnitude to substantially higher temperatures: 330K for the measured hysteresis and 390K for a presumptuous linear extrapolation of $M_s(T)$ to zero. Using the expression for the Curie constant, $C = g^2\mu_B^2 N_0 S(S+1)/3k_B$, where N_0 is the number of Mn atoms per gram Mn and k_B is the Boltzmann constant, we calculate from the slope of $\chi^{-1}(T)$, the result, $g^2S(S+1) = 410$. For $g = 2$ this implies that $S = 10$, a spin larger by a factor of four than the $S = 5/2$ of isolated Mn^{++} ions. Such a large S justifies the use of a Langevin (classical) rather than a Brillouin (quantum) functional dependence.

The data presented here not only show that room-temperature ferromagnetism is obtainable in (Ga,Mn)P:C and but also provide a meaningful confrontation with present theories [12, 13, 14, 15] describing ferromagnetism in DMS. The ferromagnetism is clearly carrier mediated [12, 13, 14, 15] and is optimized for hole-doped substrates with Mn concentrations near 3at.%. Higher concentrations of Mn are deleterious because of increased antiferromagnetic coupling [12] and a possible disorder-induced self-compensation [15]. At low Mn concentrations, RKKY interactions randomize the sign of the exchange coupling between Mn spins, and spin-glass rather than ferromagnetic behavior is expected [22].

Our experimental determination of the prefactor α discussed above allows a direct calculation of the spin

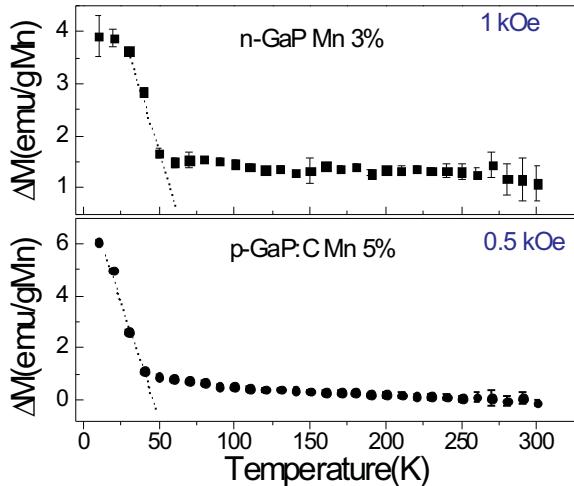


FIG. 3: Temperature dependence of the difference between field-cooled (FC) and zero-field cooled (ZFC) magnetizations (per gram Mn) for (upper panel) *n*-type GaP implanted with 3at.% Mn and (lower panel) *p*-type GaP:C implanted with 3at.% Mn. The measuring fields are indicated in the upper right hand corners of each panel.

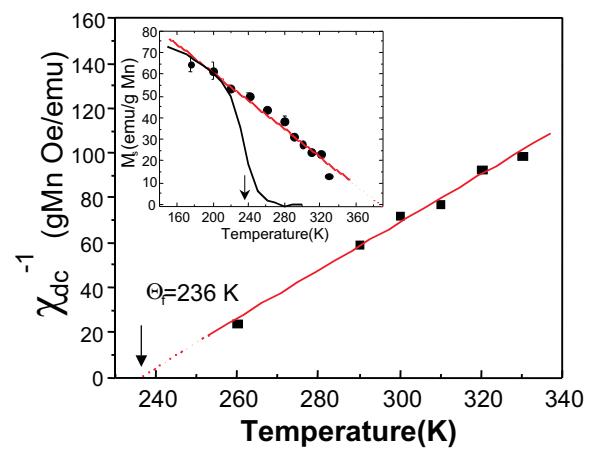


FIG. 4: Temperature dependent inverse susceptibility extrapolated (dashed line) to $\Theta_f = 236K$. The inset shows the temperature dependent "saturated magnetization" derived from fits of the field-dependent magnetization at each temperature to a Langevin function dependence as described in the text. For comparison, the solid line reproduces $\Delta M(T)$ at 1000 Oe shown in the inset of Fig. 1.

wave stiffness D , a parameter which describes the energy dispersion, $E = Dk^2$, of the spin wave excitations (magnons). We find from the thermodynamic result [23], corrected by a spin-dependent prefactor [13], the value $D = 167 \text{ meV}\text{\AA}^2$. For comparison, $D = 281 \text{ meV}\text{\AA}^2$ for Fe. Substituting $D = 167 \text{ meV}\text{\AA}^2$, $S = 5/2$, and $N_{\text{Mn}} = 1.5 \times 10^{21} \text{ cm}^{-3}$ for the volume density of Mn ions into the expression [24], $k_B T_c^{\text{coll}} = (2S+1)D(6\pi^2 N_{\text{Mn}})^{2/3}$ gives an estimate $T_c^{\text{coll}} = 385 \text{ K}$ for the upper bound on T_c due to long wavelength collective fluctuations. This value is higher than the measured $T_c = 270 \text{ K}$ and consistent with the fact that mean field theory usually overestimates the ordering temperature.

At temperatures near and above T_c , clusters in a disordered medium seem to be playing an important role [14, 15]. The presence of spin clusters is often associated [25] with a $\chi^{-1}(T)$ dependence, which approaches zero with positive curvature but which, at sufficiently high temperatures, has a linear dependence extrapolating to the paramagnetic Curie temperature, Θ_p . It is therefore reasonable to argue that at higher temperatures $\chi^{-1}(T)$ must eventually curve upwards and approach a slope four times larger than shown in Fig. 4, corresponding to $S = 5/2$ moments of the Mn ions. If so, then a linear extrapolation to $\chi^{-1}(T = \Theta_p) = 0$ would give a Θ_p considerably larger than Θ_f . As T increases beyond T_c and the ferromagnetic clusters decrease in size and number, there is a decreasing saturated moment (Fig. 4, inset) since the remaining paramagnetic regions cannot be driven into saturation without the assistance of internal Weiss fields. Disorder and proximity to a metal-insulator transition, which may be responsible for the enhanced T_c 's of the clusters [14], may also give rise to a reduced spin stiffness and the anomalously high Curie constant. Based on this evidence of ferromagnetic behavior above room temperature, it is not unreasonable to expect that even higher T_c can be obtained by further optimization of the Mn and hole dopant concentrations.

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* Electronic address: afh@phys.ufl.edu

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